Part IV

Calculation of Method B and Method C Cleanup Levels for Petroleum Mixtures

Introduction

Cleanup levels for Total Petroleum Hydrocarbon (TPH) mixtures are determined using the fractionated analytical approach. This approach divides the petroleum mixture into equivalent hydrocarbon numbers. Use of the fractionated approach requires the determination of the composition of the petroleum mixture.

Cleanup levels for petroleum mixtures are dependent on the composition of the mixture.

Method A cleanup levels for petroleum mixtures provided in Table 720-1 (Method A Ground Water Cleanup Levels), Table 740-1 (Method A Soil Cleanup Levels for Unrestricted Land Use) and Table 745-1 (Method A Soil Cleanup Levels for Industrial Land Use) are based on **assumed compositions**.

Method B and Method C cleanup levels for petroleum mixtures are based on **site-specific compositions**. Identifying the composition requires a site-specific analysis of either the contaminated medium or the source of the contamination (either the product released or another contaminated medium). See Table 830-1 for a list of contaminants to test for when establishing cleanup levels for petroleum mixtures.

Because cleanup levels for petroleum mixtures are dependent of the composition of the mixture and because the composition must be determined on a site-specific basis, **CLARC does not provide pre-calculated standard Method B or C formula values for petroleum mixtures**.

To calculate soil and ground water cleanup levels for petroleum mixtures, the assessor should use the Workbook and associated User's Guide (Publication No. 01-09-073) provided by the Department of Ecology.

Establishing Cleanup Levels for Petroleum Mixtures

Ground Water

Cleanup levels must be established for the total petroleum hydrocarbon (TPH) mixture as a whole, as well as for individual hazardous substances (TPH components) within the mixture, such as benzene, ethylbenzene, toluene, and xylene.

Under Method B and Method C, the cleanup levels for individual TPH components are established just like they would be for any other hazardous substance.

To establish a site-specific TPH cleanup level under Method B or Method C, the composition of the petroleum mixture in the ground water must be determined. Determining the composition requires the analysis of either the ground water or the source of the contamination (the product itself or contaminated soil) for petroleum fractions and other toxic components likely to be present. See Table 830-1 for a list of contaminants to test for when establishing cleanup levels for petroleum mixtures. If the analysis is based on the product or contaminated soil composition, a ground water composition must be predicted using a fate and transport model under WAC 173-340-747, such as the 3-phase or 4-phase model.

The actual or predicted ground water composition is used in Equation 720-3 to calculate a total petroleum hydrocarbon (TPH) cleanup level that takes into account the combined noncarcinogenic effects of the petroleum mixture. This TPH cleanup level may need to be adjusted downward to take into account the cleanup levels for individual petroleum components. A further adjustment may be necessary if modeling or ground water monitoring indicates biological degradation of residual petroleum would result in violation of the drinking water standards for other chemicals. This is most likely to be a concern for naturally occurring metals such as arsenic, iron and manganese that can be brought into solution by depletion of oxygen in the ground water during petroleum degradation.

See WAC 173-340-720 (4)(b)(iii)(C) and (5)(b)(iii)(C).

Surface Water

Cleanup levels must be established for the total petroleum hydrocarbon (TPH) mixture as a whole, as well as for individual hazardous substances (TPH components) within the mixture, such as benzene, ethylbenzene, toluene, and xylene.

Under Method B and Method C, cleanup levels for individual TPH components are established just like they would be for any other hazardous substance.

To establish a site-specific TPH cleanup level under Method B or Method C, the composition of the petroleum mixture in the surface water must be determined. Determining the composition requires the analysis of the surface water or the source of the petroleum contamination (the product itself or contaminated soil or ground water) for petroleum fractions and other toxic components likely to be present. See Table 830-1 for a list of contaminants to test for when establishing cleanup levels for petroleum mixtures. If the analysis is based on the source of the contamination, a water phase composition must be predicted using a fate and transport model under WAC 173-340-747, such as the 3-phase or 4-phase model.

The actual or predicted water composition is used in a risk assessment equation to calculate a cleanup level that takes into account the combined human health risk of the petroleum mixture. This equation is not specified in the regulation. However, an acceptable equation may be obtained from Ecology. This cleanup level may need to be adjusted downward to take into account the cleanup levels of the individual petroleum components.

As an alternative to calculating a site-specific TPH cleanup level, the regulation allows for the use of the applicable TPH ground water cleanup levels in Table 720-1. Use of these values would avoid the need to conduct fractionated petroleum analyses.

The cleanup levels for TPH and the TPH components must also be at least as stringent as concentrations that are protective of fish and aquatic life, as well as wildlife, just as for any other hazardous substance. Whole effluent toxicity (WET) testing may be used to demonstrate that a concentration is protective of fish and aquatic life. Other methods may need to be used to demonstrate that a concentration is protective of wildlife, if this is a concern at the site.

See WAC 173-340-730(3)(b)(iii)(C) and (4)(b)(iii)(C).

Soil

Cleanup levels must be established for the total petroleum hydrocarbon (TPH) mixture as a whole, as well as for individual hazardous substances (TPH components) within the mixture, such as benzene, ethylbenzene, toluene, and xylene.

To establish a site-specific TPH cleanup level under Method B or Method C, the composition of the petroleum mixture in the soil must be determined. Determining the composition requires the analysis of either the soil or the product released for petroleum fractions and other toxic components likely to be present. See Table 830-1 for a list of contaminants to test for when establishing cleanup levels for petroleum mixtures.

- **Direct Contact Pathway:** For petroleum mixtures, the regulation requires a concurrent evaluation of ingestion and dermal absorption. The petroleum mixture composition is used in Equation 740-3 (or, if using Method C, Equation 745-3) to calculate a protective concentration for TPH that takes into account the combined noncarcinogenic effects of the petroleum mixture. Protective concentrations for individual TPH components are established using Equations 740-4 and 740-5 (or, if using Method C, Equations 745-4 and 745-5). The

TPH concentration may need to be adjusted downward to take into account the protective concentrations for individual TPH components. See WAC 173-340-740(3)(b)(iii)(B)(III) and 173-340-745(5)(b)(iii)(B)(III).

- **Leaching Pathway:** Protective concentrations for TPH and the TPH components must be established using the methods described in WAC 173-340-747.

- **Vapor Pathway:** Since TPH and TPH components contain volatile organic compounds, the vapor pathway must be evaluated whenever one of the conditions specified in the regulation exists at a site. Protective concentrations may be determined using one or more of the methods described in the regulation.

In addition to accounting for human health impacts, soil cleanup levels for TPH and the TPH components must also account for any potential impacts to terrestrial ecological receptors (plants and animals), just as for any other hazardous substance.

Air

Cleanup levels must be established for the total petroleum hydrocarbon (TPH) mixture as a whole as well as for individual hazardous substances (TPH components) within the mixture, such as benzene, ethylbenzene, toluene, and xylene.

Under Method B and Method C, the cleanup levels for individual TPH components are established just like they would be for any other hazardous substance.

To establish TPH cleanup levels under Method B or Method C, the composition of the petroleum mixture in the air must be determined. Determining the composition requires the analysis of either the air or the source of the contamination (the product itself or contaminated soil or ground water) for petroleum fractions and other toxic components likely to be present. See Table 830-1 for a list of contaminants to test for when establishing cleanup levels for petroleum mixtures. If the analysis is based on the source of the contamination, a soil vapor composition must be predicted using a fate and transport model under WAC 173-340-747, such as the 3-phase or 4-phase model.

The actual or predicted air composition is used to calculate a total petroleum hydrocarbon (TPH) cleanup level that takes into account the combined noncarcinogenic effects of the petroleum mixture. This equation is not specified in the regulation. However, an acceptable equation can be obtained from Ecology. This cleanup level may need to be adjusted downward to take into account the cleanup levels of any individual petroleum components.

See WAC 173-340-750(3)(b)(ii)(C) and (4)(b)(ii)(C).

References Doses for Petroleum Mixtures

Petroleum products are complex mixtures that include hundreds of compounds. How to estimate the toxicity of such mixtures was subject to considerable discussion throughout the rule-making process, involving the Department of Ecology, the Department of Health, the TPH Project Oversight Group (POG), the U.S. EPA, and numerous stakeholders. Based on this work, consensus was reached on three principles:

1. Where reference doses and cancer potency factors are available for individual substances that are part of the petroleum mixture, these values should be used for these substances.
2. The remainder of the mixture should be divided into several groups of substances, or fractions, and a reference dose assigned to each fraction based on known toxicological information about substances found in those fractions or with a similar chemical structure.
3. Because of the wide range of chemicals and potential health effects, the noncarcinogenic toxicity posed by the various fractions should be assumed to be additive for the purposes of estimating the toxicity of a petroleum mixture.

Based on information developed by the National TPH Criteria Working Group, it was determined that the mixture of substances should be split into two main groups – aliphatic hydrocarbons and aromatic hydrocarbons. Each of these main groups was then further subdivided into fractions with similar physical properties.

Initial reference doses were derived from work done by the National TPH Criteria Working Group and the Massachusetts Department of Environmental Protection. At the request of EPA Region 10, the EPA's National Center for Environmental Assessment (NCEA) reviewed these values and recommended some adjustments. These recommendations were endorsed by the POG and the MTCA Science Advisory Board. These values are reproduced in the table on the next page.

Recommended References Doses
for
Petroleum Fractions and Individual Hazardous Substances

Fraction/Compound and Equivalent Carbon (EC)[1]	Surrogate	Oral RfD (mg/kg-day)	Inhalation RfD (mg/kg-day)	Source
Aliphatic EC5 to EC6	Cyclohexane	5.7	5.7	EPA
Aliphatic >EC6 to EC8	Cylcohexane	5.7	5.7	EPA
Aliphatic >EC8 to EC10	(see Note 2)	0.03	0.085	EPA
Aliphatic >EC10 to EC12	(see Note 2)	0.03	0.085	EPA
Aliphatic >EC12 to EC16	(see Note 2)	0.03	NA[3]	EPA
Aliphatic >EC16 to EC21	Mineral Oil	2	NA[3]	CWG/EPA
Aliphatic >EC21 to EC36	Mineral Oil	2	NA[3]	CWG/EPA
Aromatic EC8 to EC10	Biphenyl	0.05	0.05	EPA
Aromatic >EC10 to EC12	Biphenyl	0.05	0.05	EPA
Aromatic >EC12 to EC16	Biphenyl	0.05	NA[3]	EPA
Aromatic >EC16 to EC21	Pyrene	0.03	NA[3]	MaDEP/EPA
Aromatic >EC21 to EC36	Pyrene	0.03	NA[3]	MaDEP/EPA
n-Hexane		0.06	0.057	EPA
Benzene		0.003	0.0017	EPA
Ethyl benzene		0.1	0.286	EPA
Toluene		0.2	0.114	EPA
Xylenes		2	0.2	EPA
Naphthalene		0.02	0.00086	EPA
1,2 dibromoethane		0.000057	0.000057	EPA

Footnotes:

(1) In some cases the EPA fractions are slightly different but for consistency and simplicity they were adjusted to these which are very close (within one equivalent carbon number).

(2) The aliphatic fractions with an oral reference dose = 0.03 and an inhalation reference dose = 0.085 is based on a "mixture of alkanes" for ingestion and ATSDR chronic MRL (minimal risk level) of 0.3 mg/m3 for JP-7 as the inhalation surrogate for EC8 to EC16 which equals an inhalation RfD of 0 .085 mg/kg-day.

(3) "Volatile" is defined as EC 12 and less plus naphthalenes; therefore no inhalation reference doses are needed for higher fractions.

Abbreviations:

- NA = Not Applicable (because not volatile; see footnote 3)
- CWG = Total Petroleum Hydrocarbon Criteria Working Group
- MaDEP = Massachusetts's Department of Environmental Protection
- EPA = Environmental Protection Agency (reviews of CWG & MaDEP recommendations)